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Project Rand - Calcium and Calcium-Base Alloys.

55062

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Battelle Memorial Inst., Columbus, O.

(None)

EMAC Corp., for USAF Project MX-791 (Rand) Contr. W33-038-ac-14105

R-123

(None)

Jan 40

Unclass.

U.S.

English

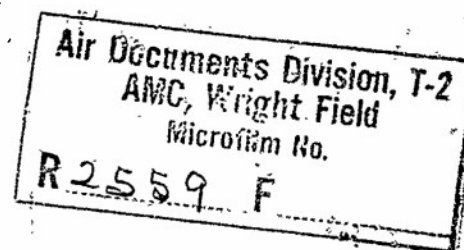
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tables, graphs

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Materials (8) Calcium alloys (19662); Project Rand
Misc. Non-Ferrous Alloys (12) (75405)

USAF C.N. W33-038-ac-14105



ATI No. 55092

U.S. AIR FORCE

Project

RAND

CALCIUM AND CALCIUM-BASE ALLOYS

BATTELLE MEMORIAL INSTITUTE • COLUMBUS, OHIO

January 1, 1949

R-123

The RAND *Corporation*
SANTA MONICA • CALIFORNIA

PROJECT RAND

CALCIUM AND CALCIUM-BASE ALLOYS

W. Hodge • R. I. Jaffee • B. W. Gonser
BATTELLE MEMORIAL INSTITUTE • COLUMBUS, OHIO

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SUMMARY

Calcium in the unalloyed condition is an extremely ductile light metal whose mechanical properties on a strength-weight basis are on a par with unalloyed aluminum. Possibilities for developing alloys for constructional use are highly doubtful.

The chief disadvantage of calcium is its poor corrosion resistance which makes it unusable in the pure form. It is believed that this could not be improved to any marked extent by alloying, so some type of cladding would be necessary. Since calcium does not alloy with iron or stainless steel, prospects for cladding with these materials are poor. Cladding with corrosion-resistant magnesium or aluminum is more promising if the boundary layer thickness of inter-metallic compound can be kept to a minimum. There are also meager possibilities for protection by coating with an organic material.

The best procedure for appraising the possibilities of calcium appears to be to try to make a strong calcium-base alloy which would then be protected by a metallic or organic coating. There is little prospect that either effort would be crowned with success.

CALCIUM AND CALCIUM-BASE ALLOYS

Purpose

The almost unlimited availability of calcium-bearing minerals and the low density of metallic calcium with its melting point higher than aluminum, indicated that a preliminary survey should be made of the possibilities for calcium and calcium-base alloys as construction materials for aircraft and guided missiles. This report contains the information and conclusions resulting from this survey.

METALLIC CALCIUM

Production

According to Mantell and Hardy⁽¹⁾ the production of metallic calcium was between 10-20 tons annually from 1920-1940, before the Electro

(1) C. L. Mantell, and C. Hardy, "Calcium, Metallurgy, and Technology", ACS Monograph No. 100, 1945.

Metallurgical Corporation started their plant late in 1939. No figures were given by Mantell and Hardy on the capacity of this plant.

The chief method formerly used for the production of metallic calcium was the electrolytic process employing a fused-salt electrolysis of anhydrous CaCl_2 at 800°C ., using graphite anodes and liners and vertical, water-cooled iron contact cathodes. This was the process used by the Electro Metallurgical Corporation at their Sault Ste. Marie plant. Another method, by which several million pounds of calcium were made during the war at the New England Lime Company, Caanan, Connecticut, employs a thermal reduction of lime by aluminum in vacuum (using the same equipment as the Pidgeon process for magnesium).⁽¹⁾

In order to produce high-purity metal from electrolytic calcium, it is necessary to refine the product by double distillation. First, the crude product is distilled below the melting point of calcium, approximately 800°C ., to free the metal from the more volatile alkali metals, especially sodium, then the main distillation is carried out at $825-850^\circ\text{C}$ which is above the melting point. Chaudron⁽²⁾ gives the following composition for electrolytic calcium before and after purification by distillation:

(1) G. C. Loomis, "Production of Metallic Calcium by Thermal Reduction", Tr. Electrochemical Society, 89, 207-216 (1945).

(2) G. Chaudron, "Calcium", Reine Metalle, p. 126, J. Springer, 1939.

<u>Electrolytic</u>		<u>Distilled</u>	
Ca metal	85.5%	Ca	99.3%
CaO	9.1%	Fe	0.02%
CaCl_2	2.7%	Cl	Traces
Si	0.35%	Si	0.14%
Fe	0.88%		
Al	0.2%		
Na + K	1.0%		

Mantell and Hardy⁽¹⁾ present figures showing that the purity of electrolytic calcium improved from 1936-1938 because of better production methods:

	<u>1936</u>	<u>1937</u>	<u>1938</u>
Ca	96.58%	97.15%	98.65%
Cl	1.95%	1.36%	0.72%
Fe	0.42%	0.37%	0.2%
Al	0.035%	0.036%	0.03%
Si	0.012%	0.01%	0.01%
Alkali metals	1.0%	0.09%	Traces

The vacuum thermal method of reduction of lime by aluminum gives a very high-purity product. The New England Lime Company⁽²⁾ give the following as the analysis of as-distilled calcium, and Everts

(1) Mantell and Hardy, loc. cit., page 34.

(2) The New England Lime Company, private communication.

and Bagley⁽¹⁾ give the following as the chemical analysis of calcium produced by that method, purified by redistillation in vacuum:

<u>Product from Retort</u>		<u>Redistilled</u>	
Mg	0.8%	Ca	99.48%
Al	0.2%	Fe	0.045%
Mn	0.035%	Mn	0.0025%
N	0.1%	Ni	0.03%
Ca (by difference)	98.865%	Cr	0.004%
		Si	< 0.002%
		Al	< .01%
		N	0.03%
		H	0.032%
		O	0.16%

Melting and Fabrication of Calcium

Molten calcium is extremely reactive and has to be protected during melting by an inert atmosphere or flux. Argon has been used as the protective atmosphere, although helium should work equally well. Nitrogen, hydrogen, or carbonaceous gases are unsatisfactory, because calcium reacts with them. No specific flux cover was mentioned for melting calcium, but eutectic mixtures of calcium chloride with other chlorides should be satisfactory, because the electrolytic process for

(1) A. H. Everts and G. D. Bagley, "Physical and Electrical Properties of Calcium", Electrochem. Soc., Presented at April, 1948, meeting in Columbus, Ohio.

calcium employs an electrolyte of fused calcium chloride, which also serves as a protective flux cover.

Melting is carried out in iron or stainless steel crucibles. Only a very small pickup of metallic impurities occurs under such conditions.

Casting of molten calcium also is done under an inert gas atmosphere, or, as is done in many cases, the ingot is solidified in the crucible.

If the calcium is sufficiently pure, fabrication by any method offers few difficulties. Ingots of the metal were easily cold rolled from 3/4-inch to 1/32-inch thickness without intermediate annealing; a cold reduction of 96 per cent⁽¹⁾. An even more impressive demonstration of the ease with which calcium may be fabricated is the extruding practice of the White Metal Rolling and Stamping Company, Brooklyn, New York⁽²⁾. This company took the crowns of distilled calcium metal produced by the New England Lime Company, Caanan, Connecticut, which were very irregular in shape, and full of voids, and extruded them at 450°-550°F. into 1½-inch rod. These rods then could be cold rolled without intermediate annealing. The extrusion temperatures used by the White Metal Rolling and Stamping Company are considerably lower than the 400°-450°C. (750°-840°F.) temperature range recommended by Bastien⁽³⁾.

(1) Everts and Bagley, loc. cit.

(2) Private communication.

(3) P. Bastien, "Properties of Sublimed Calcium", Rev. Metall., 32, Part 1, p. 132, 1935.

Mechanical Properties at Ordinary Temperature

Data on the mechanical properties at ordinary temperatures have been given by Bastien(1) and Everts and Bagley(2). They are listed in Table 1. The tensile strength of about 7000 p.s.i. for annealed calcium appears to be rather reliable. This value may be compared with other pure metals as follows:

Metal	Density	Elonga- tion, %	Tensile Strength, Annealed	Strength Weight Ratio, TS/d
Ca (sublimed, 99.5%)(1)	1.54	53	7000	4500
Mg (sublimed, 99.99%)(2)	1.74	18	35,000	20,000
Al (99.996)(3)	2.70	43-55	7000-7800	2600-2900
Al (99.5)(3)	2.70	25-35	11400-12000	4200-4400
Ti (Iodide)(4)	4.5	35	60,000	13,000
Fe (99.99)(5)	7.87	40	29,000	3700
Ni (electrolytic)(6)	8.9	49	48,000	5400
Cu (electrolytic)(6)	8.94	53	33,000	3700

The conclusions that can be drawn from these data are that pure face-centered cubic calcium has a lower tensile strength-weight ratio than the hexagonal close-packed pure metals, magnesium and titanium, but

- (1) P. Bastien, "Properties of Sublimed Calcium", Rev. Metalle, 32, Part I, page 120, 1935.
- (2) G. Chaudron, Reine Metalle, p. 119.
- (3) R. Gadeau, Reine Metalle, page 157.
- (4) I. Campbell, R. I. Jaffee, J. M. Blocher, J. Gurland, and B. W. Gonser, Electrochem. Soc., Presented at April, 1948, meeting.
- (5) H. E. Cleaves and J. M. Hiegel, J. Research, NBS 28, p. 643 (1942).
- (6) W. Broniewski and S. Kylesza, Metaux et Corrosion, 12, p. 67, 1937.

Table 1. MECHANICAL PROPERTIES OF CALCIUM

Reference	Source of Calcium	Condition	Modulus of Elasticity (psi)	Proportional Limit (psi)	Yield Strength (psi)	Ultimate Strength (psi)	Elongation (%)	Reduction of Area (%)	Hardness	Impact Value (ft-lb)	Miscellaneous
P. Bastien	Distilled	Melted under argon, as solidified	2,800,000 (loading)	1,500	-	6,250 (8-mm diam)	53 (not stated, but probably 5-cm gauge)	62	13 Brinell (2 mm, 10-kg)	22 Mesnager	Shear strength 6,100 psi
	Distilled	Extruded 8-mm wire	-	5,500	-	8,100	61 (5-cm gauge?)	68	17 Brinell	-	-
	Electrolytic	Not stated but probably as deposited	3,700,000 (pendulum)	3,100	-	7,250 (8-mm diam)	30 (5-cm gauge?)	37	14 Brinell	25 Mesnager	Shear strength 6,400 psi
	Commercial	Not stated	-	Not measured	-	4,000	Low	Low	26 Brinell	1 Mesnager	Shear strength 3,800 psi
L. Guillet	Probably distilled	Extruded wire	2,800,000	-	-	-	-	-	-	-	-
Everts and Bagley	Distilled and re-melted under argon	Worked and annealed at 400°C (5/32-in. rod)	-	-	1,990 (extension not stated)	7,000	51 (% in 1 in.)	58	Not determined	-	-
		Cold rolled (5/32-in. rod)	-	-	12,300 (extension not stated)	16,700	7 (% in 1 in.)	35	42 _H 15T	-	-

*Distilled calcium: 99.3% Ca total, 0.02% Fe, 0.14% Si, trace Cl.
 †This was a good grade of electrolytic Ca: 98.5% Ca total, 0.29% Fe, 0.07% Si, 0.85% Cl.
 ‡Commercial calcium: 86.7% Ca, 9.1% CaO, 2.7% CaCl₂ (93.9% Ca total), 0.35% Si, 0.88% Fe, 0.2% Al.
 §Same reduced with Al in vacuo, redistilled: 99.48% Ca, 0.045% Fe, 0.0025% Mn, 0.03% Ni, 0.0045% Cr, < 0.002% Si, < 0.01% Al, 0.032% N, 0.03% C, 0.032% H, 0.16% O.
 ¶The Mesnager impact specimens have the same exterior dimensions as the Charpy specimen, but the key-hole notch is made with a 2-mm diameter hole drilled on a center 1 mm from surface, instead of 5 mm from surface, as in the Charpy specimen.

that its strength-weight ratio is about the same as that of the common cubic metals, iron, nickel, copper, and aluminum. It is of interest to note that 99.5% Ca has a ratio about twice that of 99.996% Al, but about equal to that of 99.5% Al. Unfortunately, extremely high-purity calcium, equivalent to 99.996% Al, has never been prepared, and, hence, its strength is not known. It does not follow that its strength would be decreased appreciably, because the tensile strength of some metals, copper for example, is not influenced by impurities so much as aluminum.

Additional comparisons of calcium with other pure metals and some alloys, on the basis of design factors are also shown in Table 1A. In general, except for its very low modulus of elasticity (E), calcium compares favorably on a ratio of tensile or yield strength to density with either pure aluminum or pure iron, but very poorly with respect to aluminum or iron alloys. The strength of both iron and aluminum is enormously increased by alloying. On a strictly weight basis, the bending moment allowable of pure calcium is very poor for transverse loading, but, because of its low density, becomes quite satisfactory when loaded axially.

Presumably, alloys of calcium would also show greatly increased yield strength and tensile strength (favorable alloying might easily increase the yield strength 20-fold). Absolutely no information is available on the hardness or mechanical properties of calcium alloys, nor is there any indication of the probable effect of alloying on the Young's modulus value.

Table 1a. COMPARISONS OF PURE CALCIUM, PURE ALUMINUM, AND PURE IRON WITH STRUCTURAL ALLOYS OF IRON AND ALUMINUM ON THE BASIS OF DESIGN FACTORS

Design Factors	99.5% Calcium	99.9% Aluminum	2S Aluminum	24S-T Aluminum	99.99% Iron	Steel, Heat-Treated	Application
Density, lb/in. ³	0.0555	0.098	0.098	0.10	0.284	0.283	General
Modulus of elasticity (E), psi/10 ⁶	2.8	10.3	10.3	10	28.5	29.0	General
Tensile strength, psi/10 ³	7.0	6.9	13.0	64	48.0	200	General
Yield strength (0.2% offset), psi/10 ³	1.99*	1.8	5.0	40	8.1	165	General
Tensile strength, psi/density × 10 ³	126	70	132	640	169	706	Structural, general
Yield strength, psi/density × 10 ³	36	18	51	400	28.5	585	Structural, general
E/density × 10 ⁶	50	105	105	100	100	102	Beams, transverse loading
$\sqrt{E}/\text{density} \times 10^2$	305	327	327	316	188	190	Slender columns, compression
$\sqrt[3]{E}/\text{density} \times 10$	280	220	220	216	108	108	Wide columns, compression

*Extension not known, but probably 10³ cm, or approximately 4 in.

Sources: Values for pure calcium from this report.
Values for pure aluminum, 2S aluminum and pure iron calculated from data in *Mechanical Properties of Metals and Alloys*, U.S. Department of Commerce, Circular C447.
Values for 24S-T aluminum and steel from Battelle Report to Douglas Aircraft Company, Inc. (Private Communication).

The stress-strain curves reported by P. Bastien⁽¹⁾ showing a comparison between calcium, magnesium, aluminum, and lead are of little practical use, as no units of elongation are given. The curve for calcium lies between those for aluminum and lead. Bastien used cylindrical specimens, 0.315-inch (8 mm.) diameter. He notes the rate of loading as 0.157 inch (4 mm.) per minute. The gage length of the specimen is not given, but was probably 10 cm. (approximately 4 inches) from other data given. Using the experimental conditions noted, he obtained:

	<u>Ca</u>	<u>Pb</u>	<u>Al*</u>
Ultimate strength, p.s.i./10 ³	6.26	2.56	8.53
Elongation, %	53	43	25
* 99.6% Pure			

He noted that the necking down of the calcium specimens extended 2.5 cm. (about one inch) on either side of the break, compared with 1.5 cm. for aluminum and slightly more for lead. From this, he concluded long tensile specimens were necessary.

It will be noticed that the tensile strength of heavily cold-worked calcium is approximately double that of the annealed material. This again is in line with the experience with other ductile pure metals, so that the strength-weight considerations are not changed by cold working.

Concerning the two values of modulus of elasticity found by Bastien, the value of 2,800,000 p.s.i., obtained by measuring the

(1) Bastien, P., Rev. Metalurgie, 32, (1), 129 (1935).

extension between two known loads, is preferable to the value of 3,700,000 p.s.i. obtained by the pendulum method, because the loading method which was used to obtain the 2,800,000 value is closer to the usual method used. The absolute value of the modulus is low, but appears to be in line with the correlation of modulus with the melting point divided by the square of the atomic volume (calcium has a relatively large atomic volume).

No information is available on the type of impact fracture found with calcium, whether ductile or brittle. The values of 22-25 ft.-lbs. for the Mesnager specimen, which is similar to the keyhole Charpy specimen, indicate that the metal is relatively tough.

Bastien⁽¹⁾ ran hot compression tests on cylinders of calcium, 10-mm. diameter and 20 mm. high, from room temperature to 500°C. The load (units not given, but probably metric tons) required to reduce the height by 50% is shown in Curve A in Fig. 1. There is a discontinuity at 450°C., which was taken by Bastien as resulting from the allotropic modification of calcium. The high-temperature form of calcium appears to be considerably more plastic than the low-temperature form. Curve B shows the Brinell hardness of the compressed cylinders after cooling to room temperature. The recrystallization temperature appears to be between 150°C. and 300°C. from these data.

It is unfortunate that Bastien did not give the units for Curve A. If they are metric tons the compressive strength of calcium at room temperature is quite high. Assuming constant volume and a

(1) Bastien, loc. cit.

compressed cylinder of half its original height, the compressive strength at room temperature would correspond to $\frac{3500}{(.7854)(2)(10)^2} = 22 \text{ Kg./mm.}^2$ (31,500 p.s.i.). Based on the original cross section of 10 mm., the compressive strength would correspond to twice that figure. Bastien also gave data for the start of plastic flow in compression. At room temperature this amounted to 0.5 load unit. Assuming that the load was measured in metric tons, this would correspond to a compressive yield of $\frac{500}{(.7854)(10)^2} = 6.4 \text{ Kg./mm.}^2$ (9,100 p.s.i.).

General Appearance

Calcium is an alkaline earth metal closely resembling strontium and barium in its chemical behavior. When pure, it is silvery white in color, but with a whiter color than silver when freshly broken. However, it oxidizes rapidly, soon becoming covered with a white non-metallic film.

Electrical Properties

Resistivity

Temp., °C.	Resistivity, Microhm-cm.	Conductivity, % IACS	Reference
0	3.43	50.4	Goodwin, J.A.C.S., 27, p. 1403 (1905)
20	4.6	37.6	Swisher, 1917
20	4.53	38	Everts and Bagley, 1948

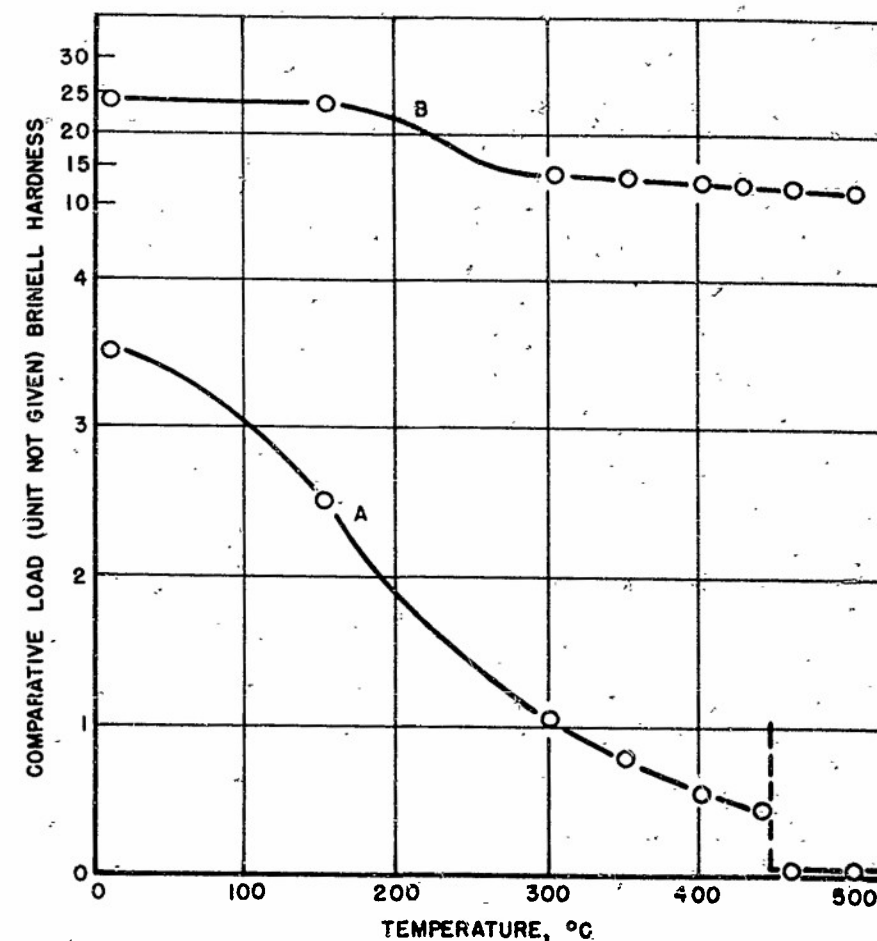


FIGURE 1. CURVE A LOADS REQUIRED TO COMPRESS CYLINDERS OF CALCIUM TO 50% OF ORIGINAL HEIGHT AT VARIOUS TEMPERATURES. CURVE B. ROOM-TEMPERATURE HARDNESS OF COMPRESSED BARS. DATA FROM BASTIAN (REV. MET. 32, 1935, 120).

The conductivity of calcium is very high on a length-weight basis: taking calcium as 100%, the conductivity of silver is 32.5% (Mantell and Hardy).

Temperature Coefficient of Resistance

Temperature Range, °C.	Coefficient	Reference
Not given	0.00457	Goodwin, J.A.C.S., 27, p. 1403, 1905

Electrochemical Equivalent

Valence	Mg./coulomb	Reference
2	0.20767	Handbook Chem. & Phys., 29th Edition

Calcium is electropositive to the alkali metals, and electro-negative to all others. Its electrode potential is -2.87 volts.

Ionization Potential

The ionization potential is given in volts for the element calcium in the atomic state. The degree of ionization is indicated by the Roman numerals: (1)

	I	II	III	IV
Volts	6.09	11.82	50.96	69.7

(1) Handbook Chem. and Phys., 26th Edition, 1942-1943.

Thermal Properties

Melting Point

Temp., °C.	Reference
851° ± 1°	Antropoff and Falk, Z, anorg. allg. Chem., 187, page 415, 1930.
810°*	International Critical Tables

* This value is undoubtedly too low.

Boiling Point

Temp., °C.	Reference
1439° ± 5°	Hartmann and Schneider, Z anorg. allg. Chem., 180, page 283, 1929.
1170°	International Critical Tables.
1240°	Handbook of Chem. and Phys., 1947, page 391, Chem. Rubber Publishing Company.

Vapor Pressure

Temp., °C.	Vapor Pressure, mm. Hg	Reference
300	9.6 x 10 ⁻⁸	Pilling, N.B., J. Inst. Metals, 25, 170 (1921).
400	4.2 x 10 ⁻⁶	
500	3.7 x 10 ⁻⁴	
600	1.2 x 10 ⁻²	
700	0.19	
800	1.8	
900	10.6	
1000	47.2	

Specific Heat

Temperature Range, °C.	Specific Heat, cal./g.	Reference
-185 to 20	0.157	Mantell and Hardy, Calcium Metallurgy and Technology
0 to 100	0.149	

Latent Heat of Evaporation

Latent Heat of Evaporation, Calories per Mole	Reference
4.53×10^{-4}	Rudberg, Phys. Rev., <u>46</u> , p. 763, 1934.

Entropy

State	Temperature, °C.	Pressure, Atmosphere	Entropy e.u.	Reference
Solid			9.95 ± 0.1	{ Kelley, K.K., Bull. No. 434, U. S. Bureau of Mines
Vapor	25	1	37.00 ± 0.01	

Linear Coefficient of Thermal Expansion

Temp. Range, °C.	Allotropic Form	Coefficient of Expansion/°C.	Reference
20-100	α	25.2×10^{-6}	{ Bastien, P., Rev. de Met., <u>32</u> , (1) page 127 (1935).
300-440	β	29.9×10^{-6}	
450-500	γ	29.9×10^{-6}	

Atomic Properties

Atomic Number

Atomic number 20

Atomic Weight

Atomic Weight 40.08 International Atomic Weights, 1942

Electronic Atomic Structure

Calcium is a normal metal in group IIA of the periodic system with two valence electrons. The electrons are arranged in orbits of 2 - 8 - 8 - 2 electrons in the K, L, M, and N shells, respectively. It exhibits a valence of two in all of its compounds, including both the oxide CaO and the peroxide CaO₂.

Principal and Secondary Quantum Numbers*

	N=1 $\underline{l=0}$	N=2 $\underline{l=0} \quad \underline{l=1}$	N=3 $\underline{l=0} \quad \underline{l=1} \quad \underline{l=2}$	N=4 $\underline{l=0}$
No. of electrons	2	2 6	2 6	2
Electron shells	2	8	8	2

* W. Hume-Rothery, "The Structure of Metals and Alloys", Institute of Metals and Monograph and Report Series No. 1, 1936, page 10.

Crystal Structure*

Type of structure	F. c. cube	C. p. hex,** $c/a=1.638$
Coordination No.	12	6,6
Lattice constants, a	5.56	3.98
		6.52
Interatomic distances, d ₁	3.93	3.98
		3.99
Goldschmidt's atomic diameter for coordination No. 12	3.93	3.98

* From Hume-Rothery, Ibid., 1936, page 41.

** The hexagonal modification of calcium is stable above 450°C., and all of the figures given in this column refer to temperatures just above the transition temperature.

A. W. Hull, Phys. Rev., 17, (2) 42 (1921) from X-ray measurements of calcium found a face-centered cubic lattice with four atoms per elementary cube, a side of which is 5.56 Å and the smallest inter-atomic distance is 3.93 Å.

Allotropic Transformation

Phase	Stable at Temperature, °C.	Observer
α	< 260*	P. Bastien, Rev. de Met., <u>32</u> , (1) page 124 (1935)
β	260-440	
γ	> 440	
<u>FCC \rightleftharpoons BCC**</u>		
α	< 450	L. Graf***, Metallwirtschaft, <u>12</u> , 649 (1933), Physik. Z. <u>35</u> , 551 (1934)
β	> 450	
<u>FCC \rightleftharpoons HCP</u>		
	Transformation temperature 430 to 450	Schulze and Overberg, Metallwirtschaft <u>12</u> , 633 (1933)

* "Despite the evidence of a transformation somewhere between 240° and 300°, the lattice type between 300° and 450° has never been definitely determined." (Mantell and Hardy, Calcium Metallurgy and Technology, Reinhold Publishing Corporation, 1945.)

** "The existence of the body-centered lattice seems to depend on impurities, and it is believed that above 450° the lattice of pure calcium is hexagonal close-packed." (Ibid.)

*** Graf used calcium 95.4% Ca.

Density:

Density	Reference
1.55(1)	Handbook of Chem. and Phys., 1947, page 391, Chem. Rubber Publishing Company
1.542 \pm 0.0005(2)	P. Bastien, Rev. de Metallurgie, <u>32</u> , (1) 127 (1935)
1.545(3)	Biltz and Wagner, Z. anorg. allg. Chem., <u>134</u> , 3 (1924)
1.540(4)	Rinck, Comp. Rend., <u>192</u> , 421 (1931)
1.48(5)	Graf, L., Metallwirtschaft <u>12</u> , 649 (1933)
1.52(6)	Physik. Z. <u>35</u> , 551 (1934)

- (1) At 20°C. referred to water at 4°C.
- (2) At 20°C.
- (3) At 25°C. referred to water at 4°C.
- (4) At 17.2°C. referred to water at 4°C.
- (5) α - calcium, wire extruded at 450°C.
- (6) β - calcium, wire extruded at 480°C.

Compressibility

The compressibility or percentage change in volume with unit change in pressure of one megabar (0.987 atmosphere, 14.504 p.s.i.) of calcium is⁽¹⁾:

$$\text{cubical, at } 30^\circ, 0 \text{ atm. } \beta = 5.885 \times 10^{-6}$$

$$\text{cubical, at } 30^\circ, 11,600 \text{ atm. } \beta = 5.300 \times 10^{-6}$$

$$\text{cubical, at } 20^\circ, 99-343 \text{ atm. } \beta = 5.8 \times 10^{-6}$$

$$\text{where } \beta = -\frac{1}{\text{vol. cm.}} \times \frac{dV \text{ (cc.)}}{dP \text{ (atm.)}}$$

at 20°, 100 to 500 megabars per sq. cm.,
compressibility = 5.7×10^{-6} (2)

- References: 1. International Critical Tables, 3, 46 (1928).
2. Richards, T. W., J.A.C.S., 37, 1643 (1915).

Chemical and Corrosion Properties

Corrosion Properties

The resistance of metallic calcium to corrosion was studied at some length by Bastien⁽¹⁾. Actually its resistance is extremely poor against most reagents. G. Chaudron⁽²⁾ has pointed out that calcium, like magnesium, is attacked by water and dilute acids by a purely chemical process. For this reason, the effect of impurities is often less marked than in many other metals. However, Bastien⁽¹⁾ says that the resublimed metal, remelted under argon, retains a brilliant white color for a long time when exposed to dry air. Exposed to humid air it becomes progressively covered with a chalky white coating, but that this corrosion is slower and a great deal more uniform than it is with more impure metal.

Using a corroding medium of one per cent hydrochloric acid (d=1.19) in 95% alcohol, Bastien obtained straight-line curves to represent the equation $P = f(t)$, where P = loss in weight of the specimen and t is the time. For the three grades of calcium he used (sublimed calcium, 99.3% Ca; electrolytic calcium 98.5% Ca; commercial Ca 86.7% Ca) the loss in weight after ten hours was found to be:

sublimed calcium: 116 mg./cm.²

electrolytic calcium: 147 mg./cm.²

commercial calcium: 120 mg./cm.²

(1) P. Bastien, "Properties of Sublimed Calcium", Rev. Metallurgic, 32, (1) 132-135 (1935).

(2) G. Chaudron, "Calcium", Reine Metalle, A.E. Van Arkel, Berlin, 1939.

The impurities in electrolytic calcium are largely metallic, while those of the commercial variety are for the most part calcium chloride and lime, which blanket the calcium crystals, retarding corrosion. Figure 2 shows graphically the results of these experiments.

Figure 3 shows the relative rate of corrosion in distilled water and various acid concentrations, as measured by the rate of gas evolution produced by a cylinder of sublimed calcium 8-mm. diameter by 8 mm. long submerged in the corroding medium.

Figure 4 is similar, but shows the volume of gas given off in the first fifteen seconds in an acid of given dilution. It is evident that sulphuric acid has a much less corrosive effect than hydrochloric or nitric because of the formation of nearly insoluble calcium sulphate which clings to the surface. Milikan⁽¹⁾ has reported the existence of several hydrated chlorides whose solubilities are different. This probably explains the sharp minimum in Curve II of Figure 3 at 0.05% HCl, since this may correspond to the formation of a hydrated chloride with a low solution rate. The rate of attack in nitric acid shows a minimum with about 5% acid and a maximum with about 75% acid concentration. Moissan⁽²⁾ and Basset and Taylor⁽³⁾ have studied the rate of attack of calcium by nitric acid; Bastien's curve confirms their findings. As in the case of the hydrated chlorides mentioned previously, the nature of the hydrated nitrates formed and the rapidity of their diffusion influence the rate of solution of the metal.

(1) Milikan, Zeit. Phys. Chem., 92-406 (1916-1918).

(2) Moissan, Annales de chim. Phys., 7-18-295 (1889).

(3) Basset and Taylor, Jour. of Chem. Soc., 101, 576 (1912).

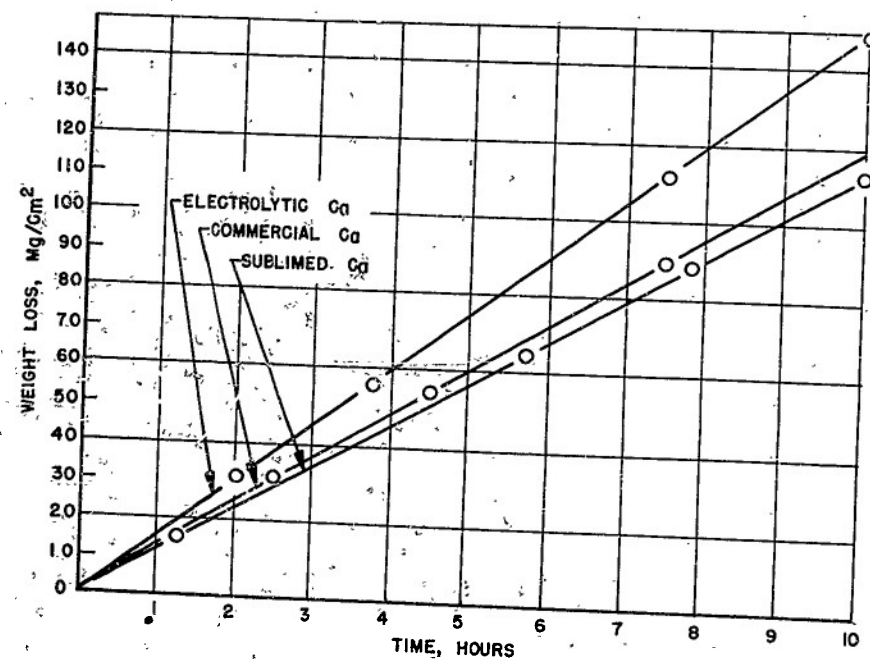


FIGURE 2. COMPARISONS BETWEEN THREE GRADES OF CALCIUM, BY MEANS OF THE THYSSÉN-SOURDOUXHE APPARATUS, IN 1% HYDROCHLORIC ACID IN ALCOHOL SOLUTION

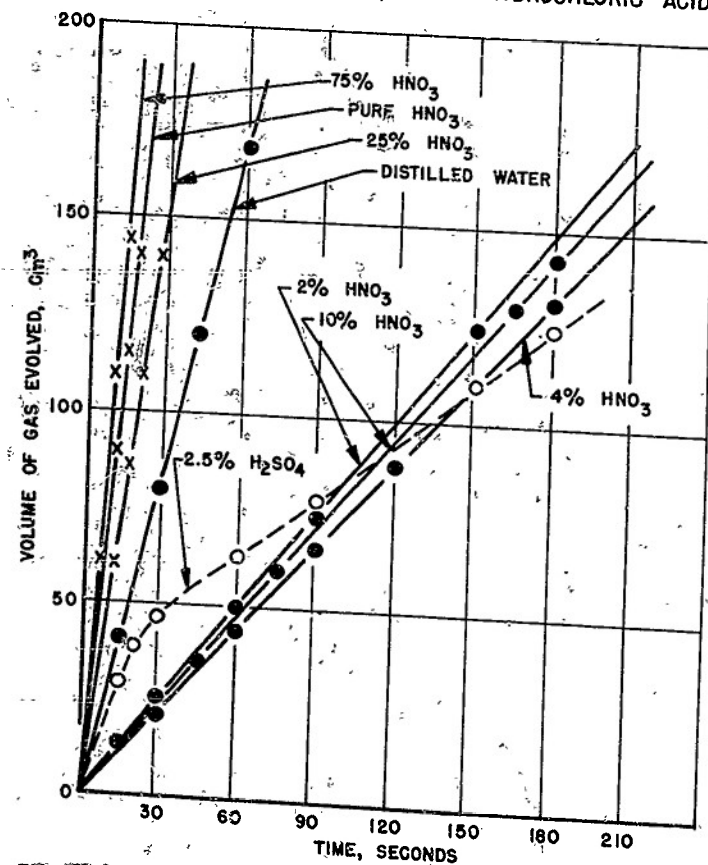


FIGURE 3. CURVES OF GAS EVOLUTION AS A FUNCTION OF TIME

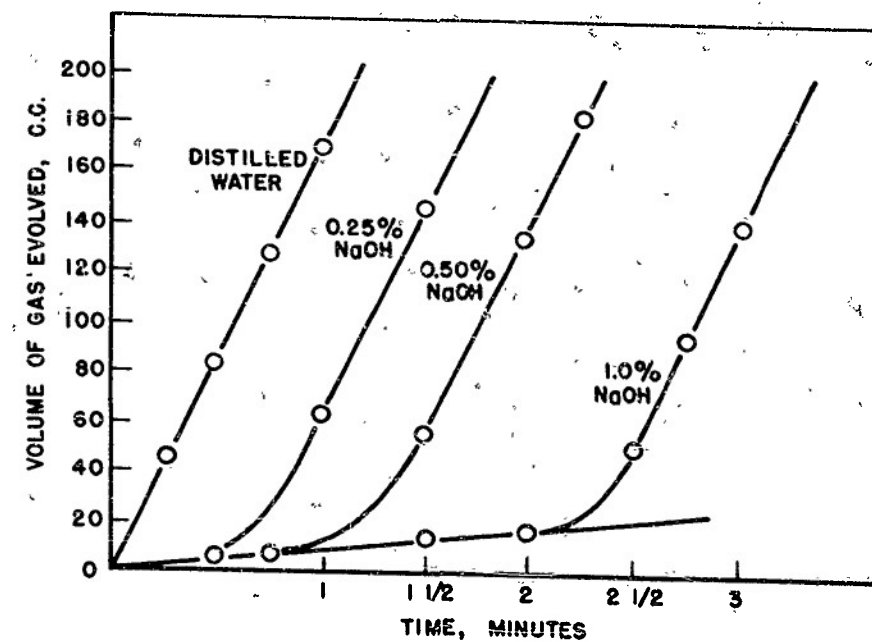


FIGURE 4. GAS EVOLUTION AS A FUNCTION OF TIME: SUBLIMED CALCIUM ATTACKED BY DILUTE SOLUTIONS OF CAUSTIC SODA

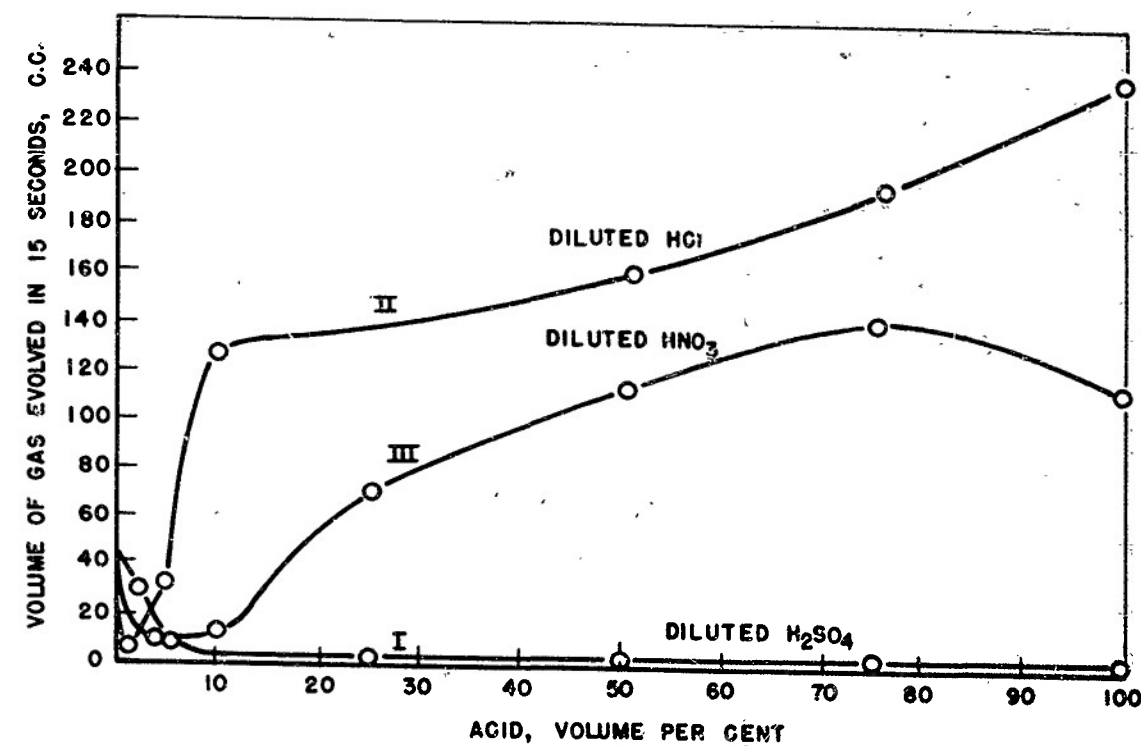


FIGURE 5. RATE OF ATTACK ON SUBLIMED CALCIUM IN AQUEOUS SOLUTIONS OF MINERAL ACIDS

Figure 5 shows the results of a similar study of the rate of attack in solutions of sodium hydroxide. In solutions containing 100% to 10% by volume of hydroxide, the rate of attack is slow. In from 10% to 0% caustic soda solutions the rate of attack increases as pure water is approached, and, somewhat curiously, in dilute solutions the rate of attack begins slowly and then accelerates to equal that obtained in distilled water.

In general, the resistance to corrosion of metallic calcium is poor against water, moist air, all acids, and dilute alkalies.

Miscellaneous Chemical Properties

Calcium and carbon react exothermically when heated together to form calcium carbide (CaC_2), a white solid when pure⁽¹⁾.

Calcium metal does not react with dry oxygen at room temperature, but combines rapidly at 300°C. or above. Similarly, it reacts slowly with dry nitrogen at 300°C., but the reaction becomes rapid at 900°C.

Dry chlorine or bromine does not attack the metal at room temperature, but the reaction becomes violent at 400°C. or above.

The hydride, CaH_2 is rapidly formed with hydrogen at 400°C. with evolution of heat. Higher yields of CaH_2 are obtained at lower temperatures (250°C. is optimum), although the reaction rate is slower.

(1) Mantell and Hardy, "Calcium Metallurgy and Technology", Reinhold Publishing Corporation, New York

The avidity with which calcium reacts with water is made use of to remove the last traces of water from absolute alcohol. Also, when very high vacuum is desired, metallic calcium, heated in a tube connected to the evacuated system, takes up the oxygen and nitrogen, thus reducing the pressure in the system to very low values. Calcium does not take up argon; hence it is used to separate argon from nitrogen. It reacts in moist CO_2 to form calcium carbonate, but when rapidly heated in CO_2 , lime and calcium carbide are formed. Heated in ammonia, calcium forms the hydride and nitrogen. In the cold, calcium reacts exothermically with ammonia to form $\text{Ca}(\text{NH}_2)_2$, which is converted to $\text{Ca}(\text{NH}_2)_2$ in the absence of air.

A large number of natural compounds of calcium exist, of which limestone (CaCO_3) is the most important.

Liddell⁽¹⁾ mentions the following compounds; calcium bisulphate, bromide, carbide, chlorate, carbonate, chloride, fluoride, hydroxide, hydride, iodide, nitrate, nitride, oxide, phosphate, sulphate, sulphide, sulphite, and tungstate as having some commercial application.

ALLOYS OF CALCIUM

Fundamental Considerations

Size Considerations

Calcium has a large atomic size, the face-centered cubic form having an interatomic distance of 3.93 angstroms at room temperature, (1) Liddell, Handbook of Nonferrous Metallurgy, McGraw-Hill Book Co., Inc., New York.

and the high-temperature hexagonal-close-packed allotrope having an interatomic distance of 3.98 just above 450°C. The bulk of metallic atoms have interatomic distances located between 2.3 and 3.0 angstroms, which are too small for extensive formation of solid solutions, according to Hume-Rothery's size factor rule.

Table 2 lists the interatomic distances of the elements and their differences from the interatomic distance of calcium.

Substitutional Solid Solutions. Using the customary ± 15 per cent difference in interatomic distance as a criterion of a good-size fit, the only elements which are close enough to calcium in atomic size to be expected to form solid solutions in calcium are the following:

Misch metal	barium	+10%
	cerium	-7.5%
	lanthanum	-5%
	lead	-11%
	strontium	+9%
	thallium	-13%
	yttrium	-8%

Borderline cases, between 15 and 20 per cent difference in atom sizes, are the following:

hafnium	-19%
indium	-20%
potassium	+18%
zirconium	-19%

Interstitial Solid Solutions. It is customarily believed that only transitional metals (those metals with unpaired d-electrons in their inner orbit) form interstitial solid solutions, and these with small elements whose interatomic distances are 0.59 or less than that of the

Table 2. ATOMIC SIZE OF THE ELEMENTS

Element	Periodic Position		Crystal Structure		Interatomic Distance*		
	Period	Group	Kind	Coordination (Nearest Neighbors)	d, Angstroms	Difference From Calcium %	Ratio to Calcium
Aluminum	2nd short	III-B	FCC	12	2.86 (incompletely ionized)	-27	0.73
Antimony	2nd long	V-B	Rhomb	3-3	2.70 (fully ionized)	-31	0.69
Arsenic	1st long	V-B	Rhomb	3-3	2.9, 3.36	-26, -15	0.74, 0.86
Barium	3rd long	II-A	BCC	8	2.51, 3.15	-36, -20	0.64, 0.80
Beryllium	1st short	II-B	HCP	12	4.34	+10	1.1
Bismuth	3rd long	V-B	Rhomb	3-3	2.25	-43	0.57
Boron	1st short	III-B	?	?	3.11, 3.47	-21, -13	0.79, 0.88
Cadmium	2nd long	II-B	HCP	12	1.8 (est)	-53	0.46
Calcium	1st long	II-A	FCC < 450°C HCP > 450°C	12	3.04	-23	0.77
Carbon	1st short	IV-B	Diam	4	3.93	0	1.00
Cerium	Rare Earth		HCP, FCC	12	1.54	-61	0.39
Chromium	1st long	VI-A	BCC	8	3.64	-7.5	0.93
Cobalt	1st long	VIII-A	HCP, FCC	12	2.49	-37	0.66
Copper	1st long	I-B	FCC	12	2.50	-36	0.64
Gallium	1st long	III-B	Orthorhombic	12	2.55	-35	0.65
Germanium	1st long	IV-B	Diam	4	2.44	-38	0.62
Gold	3rd long	I-B	FCC	12	2.45	-38	0.62
Hafnium	3rd long	IV-A	HCP	12	2.88	-27	0.73
Hydrogen	1st short	I	?	?	3.17	-19	0.81
Indium	2nd long	III-B	FCC	4-8	0.46	-88	0.12
					3.14	-20	0.80

*Values of interatomic distance taken from Hume-Rothery, *Structure of Metals and Alloys*, pp. 40-48, except for hydrogen, nitrogen, and oxygen which were taken from N.N. Engel, "Some New Viewpoints on the Metallic Bond" (as yet unpublished).

Table 2. (Cont'd)

Element	Periodic Position		Crystal Structure		Interatomic Distance*		
	Period	Group	Kind	Coordination (Nearest Neighbors)	d, Angstroms	Difference From Calcium %	Ratio to Calcium
Iridium	3rd long	VIII-B	FCC	12	2.71	-31	0.69
Iron	1st long	VIII-A	BCC	8	2.48	-36	0.63
Lanthanum	3rd long	III-A	FCC	12	3.74	-5	0.95
Lead	3rd long	IV-B	FCC	12	3.49	-11	0.89
Lithium	1st short	I-A	BCC	8	3.04	-23	0.77
Magnesium	2nd short	II-B	HCP	12	3.2	-18.5	0.81
Manganese	1st long	VII-A	Complex cubic	6	2.5 (approx)	-36	0.64
Mercury	3rd long	II-B	Rhomb	8	3.0	-23	0.76
Molybdenum	2nd long	VI-A	BCC	12	2.72	-30	0.69
Nickel	1st long	VIII-C	FCC	12	2.49	-36	0.63
Niobium (Columbium)	2nd long	V-A	BCC	8	2.86	-27	0.73
Nitrogen	1st short	V	?	?	1.42	-64	0.36
Osmium	3rd long	VIII-A	HCP	12	2.70	-31	0.69
Oxygen	1st short	VI	?	?	1.32	-66	0.34
Palladium	2nd long	VIII-C	FCC	12	2.75	-38	0.70
Phosphorus	2nd short	V-B	Rhomb	3-3	1.74, 3.01	-56, -23	0.44, 0.77
Platinum	3rd long	VIII-C	FCC	12	2.77	-30	0.71
Potassium	1st long	I-A	BCC	8	4.62	+18	1.18
Rhenium	3rd long	VII-A	HCP	12	2.75	-30	0.70
Rhodium	2nd long	VIII-B	FCC	12	2.68	-32	0.66

*Values of interatomic distance taken from Hume-Rothery, *Structure of Metals and Alloys*, pp. 40-48, except for hydrogen, nitrogen, and oxygen which were taken from N.N. Engel, "Some New Viewpoints on the Metallic Bond" (as yet unpublished).

Table 2. (Cont'd)

Element	Periodic Position		Crystal Structure		Interatomic Distance*		
	Period	Group	Kind	Coordination (Nearest Neighbors)	d, Angstroms	Difference From Calcium %	Ratio to Calcium
Rubidium	2nd long	I-A	BCC	8	4.87	+24	1.24
Selenium	1st long	VI-B	Hex	2-4	2.32, 3.46	-41, -12	0.59, 0.88
Silicon	2nd short	IV-B	Diam	4	2.35	-40	0.60
Silver	2nd long	I-B	FCC	12	2.88	-27	0.73
Strontium	2nd long	II-A	FCC	12	4.29	+9	1.09
Tantalum	3rd long	V-A	BCC	8	2.86	-27	0.73
Tellurium	2nd long	VI-B	Hex	2-4	2.86, 3.46	-27, -12	0.73, 0.88
Thallium	3rd long	III-B	HCP, FCC	12	3.42	-13	0.87
Tin	2nd long	IV-B	Diam	4	2.98	-24	0.76
Titanium	1st long	IV-A	Tetrag	4-2	3.02, 3.17	-23, -19	0.77, 0.81
			HCP	12	2.95	-25	0.75
			BCC	8	2.88	-27	0.73
Tungsten	3rd long	VI-B	BCC	8	2.74	-30	0.70
Vanadium	1st long	V-A	BCC	8	2.61	-34	0.66
Yttrium	2nd long	III-A	HCP	12	3.63	-8	0.92
Zinc	1st long	II-B	HCP	12	2.75	-30	0.70
Zirconium	2nd long	IV-A	HCP	12	3.19	-19	0.81
			BCC	8	3.13	-20	0.80

*Values of interatomic distance taken from Hume-Rothery, *Structure of Metals and Alloys*, pp. 40-48, except for hydrogen, nitrogen, and oxygen which were taken from N.N. Engel, "Some New Viewpoints on the Metallic Bond" (as yet unpublished).

metals themselves. For the transition metals these small atoms are the metalloids, carbon, nitrogen, hydrogen, and oxygen.

Since calcium has a very large atom size, it may be possible that some of the small metallic atoms will form interstitial solid solutions with it. The last column in Table 2 lists the ratios of the interatomic distances of the elements to that of calcium. These elements in the order of increasing ratio are:

hydrogen	0.12
oxygen	0.34
nitrogen	0.36
carbon	0.39
boron	0.46
beryllium	0.57
silicon	0.60

There is only a slight possibility that these elements can go into solution in calcium.

Valence Considerations

According to Hume-Rothery's relative valency rule, other things being equal, the solid solubility of metals with electronic valences (number of electrons in outer orbit) higher than calcium should be larger in calcium than the solid solubility of calcium in them. Calcium has an electron valence of two. Thus, the solid solubility of lead in calcium should be higher than the solid solubility of calcium in lead.

Electronic Bonding Considerations

Calcium has a normal electronic structure, and is bonded together by purely metallic electron bonds. Therefore, it cannot be expected to alloy well with the transitional elements, which have unpaired d-electrons inside of the valency electrons, and are bonded by d-bonds as well as metallic bonds. In other words, the exchange forces between the atoms would be broken if extensive alloying took place between calcium and transitional metals. This eliminates metals like iron, nickel, titanium, zirconium, columbium, tantalum, chromium, molybdenum, etc., from consideration as potential alloying elements with calcium.

Alloy Systems*

Silver-Calcium Alloys

The constitution diagram of the silver-calcium alloys according to Hansen⁽¹⁾ is shown in Figure 6. This shows a eutectic at 60.5% Ca, melting point 470°C. with no solid solubility and a compound at 47% Ca (AgCa_2). At the silver end there is no solid solubility and a eutectic at 5.7% Ca, melting point 653°C. between silver and Ag_4Ca . Mantell and Hardy,⁽²⁾ quoting Degard⁽³⁾ note that an X-ray study of the silver-calcium system gave no indication of the compounds AgCa_2 , Ag_2Ca , or Ag_4Ca . The compounds AgCa (face-centered cubic, with $a = 9.07\text{\AA}$)

* Numbers in () refer to references at end of section.

and Ag_3Ca (tetragonal, with $c/a = 0.88$ and $c = 9.96\text{\AA}$) were found. The diagram as given was constructed by Baar⁽⁴⁾ from thermal and microscopic measurements, and appears to have been checked by Kremann, Wostall and Schöpfer⁽⁵⁾ by potential measurements. No real investigation of the solid solubility relations at either end of the diagram has been made. There remains a possibility of considerable solid solubility at the calcium end of the series.

It seems probable that the compounds formed are ionic and would make no useful alloys.

Some commercial applications of the 2.5% and 3% Ca alloys have been made in electrical contacts. Little is known of the high-calcium alloys.

Aluminum-Calcium Alloys

The aluminum-calcium diagram from Hansen⁽¹⁾ is shown in Figure 7. The diagram shows two eutectics, one at 73% Ca (melting point 545°C .) and one at 7.55% Ca (melting point 616°C .) and two compounds, Al_2Ca (42.62% Ca) and Al_3Ca (33.02% Ca). The latter has a suppressed maximum, decomposing at 700°C . to liquid and Al_3Ca . The latter compound melts at 1079°C . and is unusually stable. Nowotny, Wormnes, and Mohrheim⁽⁶⁾ assumed that what is supposed to be Al_3Ca is a peritectically formed mixture of Al_2Ca plus aluminum, but Einerl and Neurath^(6a) report the existence of Al_3Ca . The diagram as given is from Matsuyama⁽⁷⁾ and practically checks an earlier determination by Donski⁽⁸⁾ except

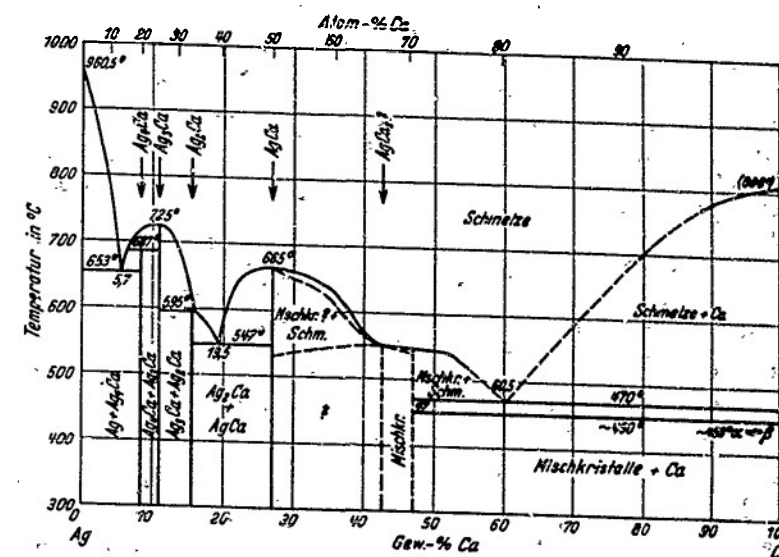


FIGURE 6. THE SILVER-CALCIUM SYSTEM, ACCORDING TO BAAR⁽⁴⁾

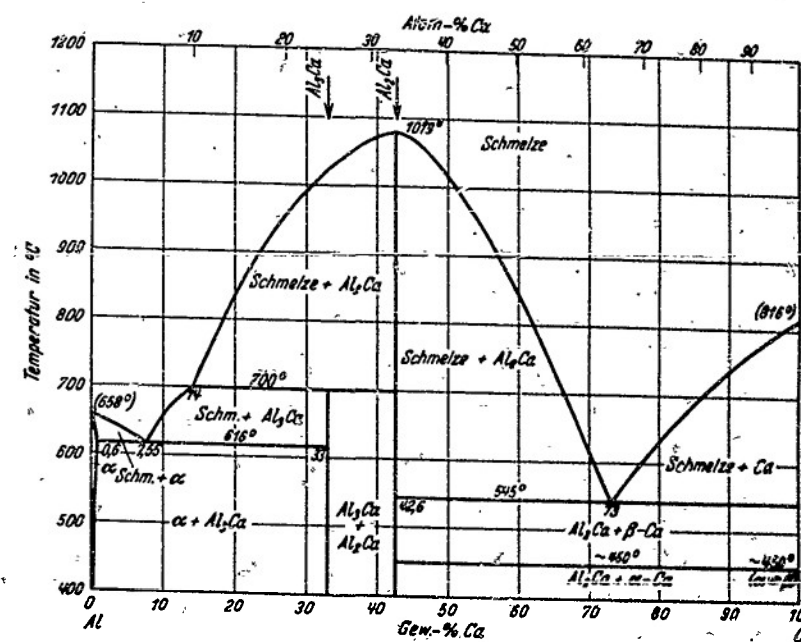


FIGURE 7. THE ALUMINUM-CALCIUM SYSTEM, ACCORDING TO HANSEN⁽¹⁾

that the latter placed the high-aluminum eutectic at 610°C. and the decomposition point of Al_3Ca at 692°C. Matsuyama shows a solid solubility of calcium in aluminum of 0.6% at 616°C., falling to 0.3% at room temperature. No solid solubility of aluminum in calcium is reported.

Mantell and Hardy⁽²⁾ list a large number of patents of aluminum alloys containing up to 2% calcium, and the list is still incomplete. No use has been suggested for high calcium-aluminum alloys.

Arsenic-Calcium Alloys

Calcium arsenide, Ca_3As_2 (44.5% Ca) was prepared by Lebeau⁽⁹⁾ by direct synthesis and also by reduction of calcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$, with carbon, in 1899. Available literature contains no other reference to this alloy system.

Gold-Calcium Alloys

The binary alloy diagram, Fig. 8, p.37, from Hansen,⁽¹⁾ prepared by Weibke and Bartels⁽¹⁰⁾ shows a series of six compounds with four eutectics. At the calcium end of the diagram, considerable solubility (about 11%) of gold in calcium is indicated and a eutectic at about 87.5% Ca melting at 658°C. The compounds AuCa_3 (28.92% Ca) and Au_3Ca_4 (21.32% Ca) both have suppressed maximums. The highest melting compound (melting point 1015°C.) occurs at 18.43% Ca, corresponding to $\text{Au}_9\text{Ca}_{10}$. The authors were quite certain that this was not AuCa (16.89% Ca). The effect of gold on the inversion point of calcium at

450°C. was not investigated. More work is needed at the calcium end of this system for confirmation and revision.

Boron-Calcium Alloys

Little is known of this series. Hansen⁽¹⁾ quotes Stackelberg and Neumann⁽¹¹⁾, saying the boride of calcium has the formula CaB_6 with a cubic CsCl structure and a B_6 space group (one molecule in elementary cell). They state that the metallic character is evident from the electrical conductivity.

Mantell and Hardy⁽²⁾ give the melting point of calcium boride as about 2000°C. It does not react with water, hydrochloric or hydrofluoric acids, but is decomposed slowly by concentrated sulphuric acid and energetically by nitric acid. The compound scratches quartz easily and is just able to scratch rubies. Kroll and Jensen⁽¹²⁾ have prepared the pure compound and state that it has nearly the theoretical composition 61.84% boron, 38.16% calcium, and its density is 2.42. It is claimed to be an effective deoxidizer for steel, copper, and their alloys.

Barium-Calcium Alloys

An X-ray investigation of this system was reported by Klemm and Mika⁽¹³⁾. They found a wide range of solubility of calcium in barium, the maximum being 63.4% Ca. A narrow two-phase field extends from 63.4% to 68.8% Ca, and the maximum solubility of barium in calcium is 31.2% Ba.

From the limited data given, it is probable that the melting points of all of the alloys do not vary widely from those of the components (Ca 851°C. and Ba 704°C.). Although a wide series of single-phase alloys is indicated, it is extremely unlikely that the corrosion resistance would be at all good, since both components exhibit very good chemical activity.

Beryllium-Calcium Alloys

Kroll and Jess⁽¹⁴⁾ made an alloy of 26.7% calcium, 71.2% beryllium by dropping a piece of beryllium into molten calcium held in a magnesia crucible under an argon atmosphere. They obtained a button with a beryllium core and an alloy coating of the composition given. The alloy was very brittle.

From the foregoing description, there appears to be small likelihood of any useful alloys of beryllium in calcium. Since the melting point of beryllium is well above the boiling point of calcium, alloys would be difficult to prepare unless the beryllium dissolved readily in the calcium, which does not appear to be the case. As structural materials, calcium-base alloys with beryllium do not appear promising.

Bismuth-Calcium Alloys

The bismuth-calcium system shown throughout the entire range by Hansen⁽¹⁾ is taken from the work of von Kurzyniec⁽¹⁵⁾. Von Kurzyniec's diagram is shown in Figure 9. His calcium probably contained nitrogen

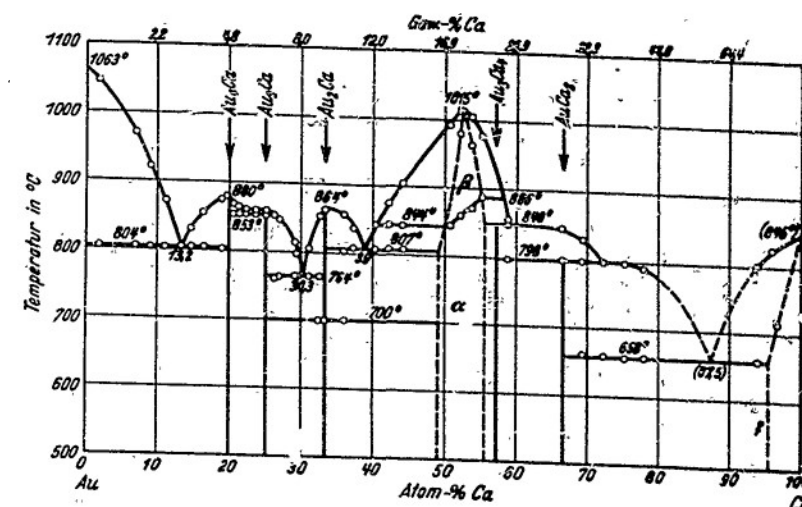


FIGURE 8. THE GOLD-CALCIUM SYSTEM, ACCORDING TO WEIBKE AND BARTEL⁽¹⁰⁾

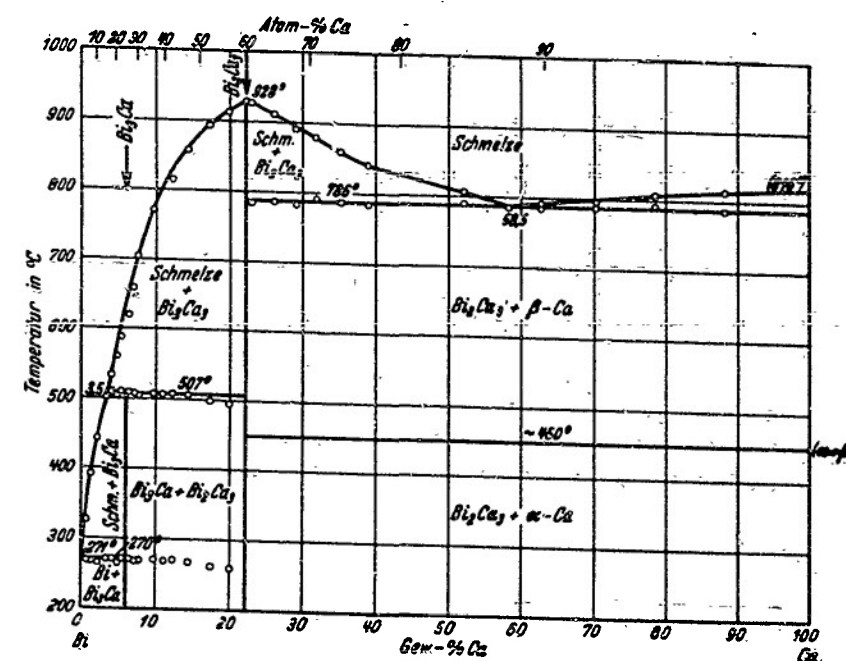


FIGURE 9. THE BISMUTH-CALCIUM SYSTEM, ACCORDING TO VON KURZYNIEC⁽¹⁵⁾

lowering the melting point to 816°C . In consequence, the true temperature of the Bi_2Ca_3 - Ca eutectic presumably is above 786°C . Donski⁽¹⁶⁾ placed the eutectic between bismuth and undefined crystals at 265°C , instead of 270°C . (but he gave the melting point of bismuth as 268°C , in place of 271°C .) and the peritectic at 498°C . in place of von Kurzynies's 507°C .

No data are given to show the limit of solid solubility of bismuth in calcium, nor the relative stability of the high-calcium alloys.

Carbon-Calcium Alloys

Carbon and calcium heated together react exothermically to form calcium acetylide, CaC_2 , universally called calcium carbide (which does not exist). CaC_2 is a white (when pure) nonmetallic solid which reacts with water to form acetylene (C_2H_2) and lime (CaO).

No data exist on any other alloys. No useful metallic alloy would be expected.

Calcium-Cadmium Alloys

Hansen⁽¹⁾ gives the diagram of Fig. 10, p. 40 to illustrate the phase relationships of the alloys of calcium and cadmium. Taken from the work of Donski⁽¹⁷⁾, it is entirely indeterminate in the high-calcium end. Donski used a rather impure calcium containing 0.55% Al, 0.28% SiO_2 , and unknown nitrogen, melted in Jena glass tubes without argon protection. The high-calcium alloys reacted with the tube and contained

high nitrogen content. Donski predicted an appreciable solubility of cadmium in calcium from the extent of the eutectic line at 415°C , which he was able to detect by thermal arrests.

From a theoretical standpoint, more work is needed in this system. From the standpoint of corrosion resistance, the alloys appear unpromising, even if the melting point of the eutectic were considered high enough to make the alloys valuable.

Calcium-Cerium Alloys

The alloys of calcium with cerium are hard, white, stable in air, and strongly pyrophoric, according to Smith Hopkins⁽⁶⁵⁾. The calcium content of these alloys is not given. Nowotny⁽⁶⁴⁾ gives X-ray lattice constants for CaNi_5 and LaNi_5 . For CeNi_5 , $a = 4.864$, $c/a = 1.644$, $d = 8.74$; for LaNi_5 , $a = 4.952$, $c/a = 1.616$, $d = 8.37$. Cerium is one of the elements whose atomic volume is a close match for calcium, making alloying possible. Some further study of this system is desirable.

Calcium-Copper Alloys

Although the Institute of Metals bibliography of the constitution of alloys⁽¹⁸⁾ gives a number of later references, no new diagram has been made since that of Baar⁽¹⁹⁾ in 1911, here taken from Hansen⁽¹⁾ and shown as Figure 11. All of the later work is at the

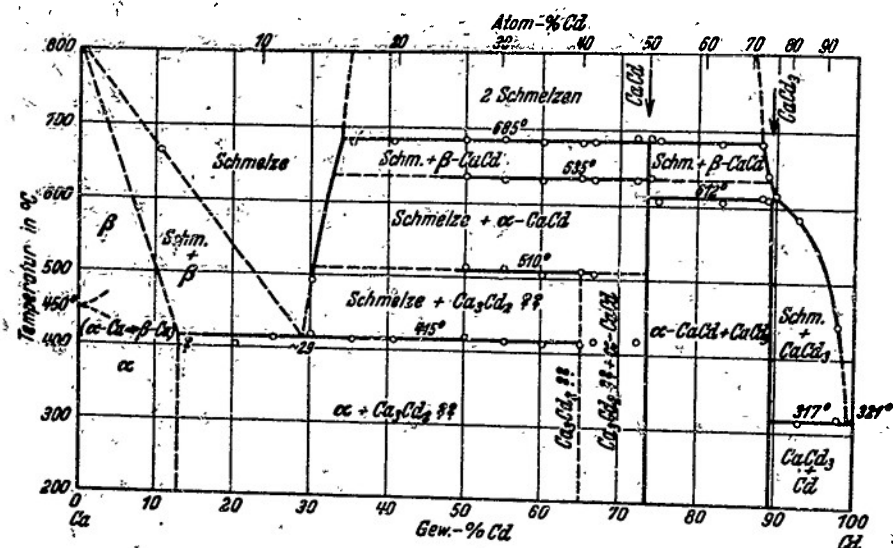


FIGURE 10. THE CALCIUM-CADMIUM SYSTEM, ACCORDING TO DONSKI (17)

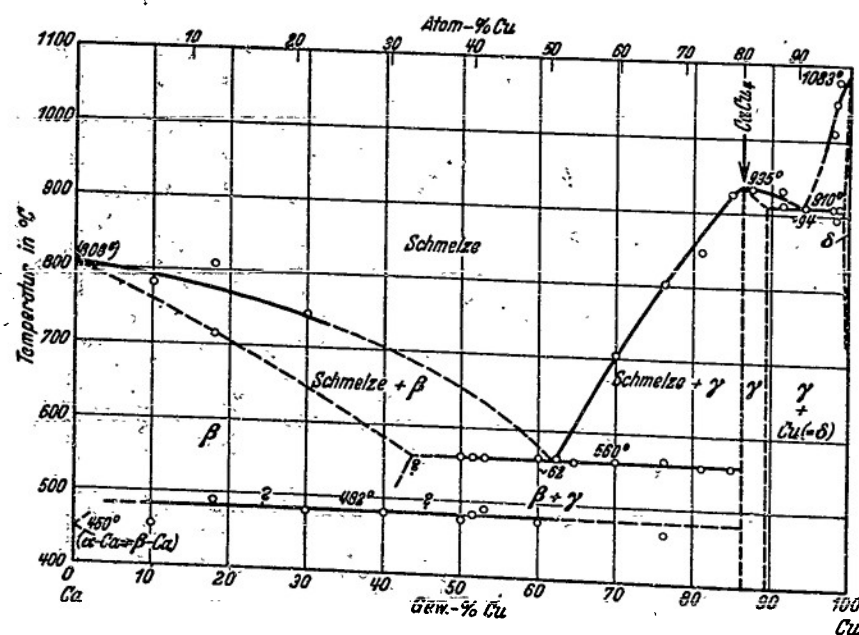


FIGURE 11. THE CALCIUM-COPPER SYSTEM, ACCORDING TO BAAR (19)

copper end of the diagram, where the alloys have considerable commercial importance. The eutectic at about 38 per cent calcium (melting point 560°C.) is between calcium and the compound CaCu_4 . The eutectic alloy is quite brittle. There appears to be considerable solid solubility of CaCu_4 in calcium. Baar found the inversion point of calcium raised to 482°C. $\pm 7^\circ\text{C}$. between 90% calcium and 40% calcium. Below 40% calcium the inversion point line on the diagram is indefinite.

Haucke (20) found the intermetallic compound was CaCu_5 , not CaCu_4 , by X-ray determination of the structure.

The probability of finding a useful high-calcium alloy in this system is based on the validity of the extensive solubility of copper in beta-calcium reported by Baar. Even if the alloy were useful, it still may have poor corrosion resistance.

Calcium-Iron Alloys (1)

Quasebart (21) and Watts (22) were each unable to alloy calcium with liquid iron. Attempts to interdiffuse calcium and iron at 750°C.-770°C. and at 850°C.-880°C. were also unsuccessful. Watts said definitely that iron and calcium do not alloy. Ledebur (23), Stockem (24), and Wener (25) also obtained negative results in attempts to make calcium-iron alloys.

Calcium-Mercury Alloys

Hansen⁽¹⁾ shows two rather different constitution diagrams in the range of 90% mercury and over, but does not discuss high-calcium alloys of this system at all, apparently because the mercury boils off before alloying.

Calcium-Lithium Alloys

The equilibrium diagram of calcium-lithium alloys was investigated by Zamotorin⁽²⁶⁾, who made cooling curves using a special furnace with an argon atmosphere and a Kurnakow pyrometer. He determined a peritectic $\text{Ca} + \text{liquid} \rightarrow \text{Ca}_2\text{Li}$ at 225°C. Ca_2Li and Li form a eutectic mixture at 165°C. The maximum hardness corresponds to Ca_2Li . Nothing is reported about the stability of these alloys.

The diagram corresponds to Type IIIb in Jänecke's⁽²⁷⁾ system of classification of equilibrium diagrams.

(Zamotorin's original article is not available.)

Calcium-Magnesium Alloys

The calcium-magnesium system has been investigated in certain ranges by many authors, but the only available data for the high-calcium end of the system are those of Baar⁽²⁸⁾ and Hansen⁽¹⁾, which are shown in Fig. 12, p. 45. Baar used calcium with 0.55% Al - Fe, 0.28% Si, and unknown, but presumably rather high nitrogen, and made his melts under hydrogen in Jena glass tubes. As a result of this technique,

considerable error in temperatures is probable at the high-calcium end. He did not investigate the solid solubility of Ca_3Mg_4 either in calcium or magnesium. Haughton⁽²⁹⁾ has shown 1.8% calcium dissolves in magnesium at 517°C. and 0.5% at 250°C. Quite similar results were reported by Nowotny, Wormnes, and Mohrheim⁽³⁰⁾. Loomis⁽³¹⁾ reports that a few per cent of magnesium in calcium hardens the metal and stabilizes it somewhat.

Only one compound is formed, determined as Ca_3Mg_4 (melting point 720°C.) by Baar. The existence of this compound was confirmed by Kremann, Wostall, and Schöpfer⁽³²⁾. Paris⁽³³⁾ believes the compound is Ca_3Mg_5 (50.3% Mg) instead of Ca_3Mg_4 . However, Vosskuhler⁽³⁴⁾, by thermal analysis and micrographic examinations of calcium-magnesium alloys with up to 60% Ca, found only one compound Mg_2Ca (melting point 714°C.). A eutectic between this compound and magnesium was placed at 16.3% Ca (melting point 516°C.). A eutectic melting point between Mg_2Ca and Ca was determined at 445°C. He reported the solubility of calcium in magnesium as 0.18% at 300°C., 0.29% at 400°C., 0.66% at 500°C., and 0.78% at the eutectic, or considerably less than was found by Haughton.

Although magnesium additions cannot be expected to form stable alloys with calcium, the addition of magnesium in amounts of less than 10% (so as not to depress the melting point unduly) might be quite desirable in an alloy to be protected by cladding with a stable metal or plastic coating.

Calcium-Nickel Alloys

Information on this system of alloys is very incomplete, and the solubility is probably similar to that of iron. Nowotny⁽⁶⁴⁾ gives X-ray lattice constants for CaNi_5 : $a = 4.952$, $c/a = 1.616$, $d = 8.37$. The addition of small amounts of calcium with other elements, particularly zirconium and aluminum, to nickel alloys is said to increase the useful life of high-resistance, high-temperature alloys. Calcium is useful as a deoxidizing agent for nickel (calcium-silver alloy with or without cerium is used).⁽⁶⁶⁾

Calcium-Nitrogen Alloys and the Melting Point of Pure Calcium

Nitrogen combines with calcium to form the compound Ca_3N_2 with 18.90% N. The melting point of the compound is 1195°C ., according to Antropoff and Falk⁽³⁵⁾, whose partial diagram is given in Hansen⁽¹⁾, and is shown in Figure 13. A eutectic with 2.2% N melts at 780°C .

Unfortunately, most of the data on calcium given in the literature do not take into account the marked lowering of the melting point of calcium by a small amount of nitrogen which is almost always present as an impurity. The Chemical Rubber Handbook⁽³⁶⁾ in at least all editions up to the 30th (1947), as well as most available tables in English give the melting point of calcium as 810°C . Hume-Rothery⁽³⁷⁾ determined the melting point as 820°C . by melting the purest calcium he had available in an alundum crucible under argon containing 10% nitrogen. He apparently did not appreciate the notable depressing effect on the melting point of a small amount of nitrogen.

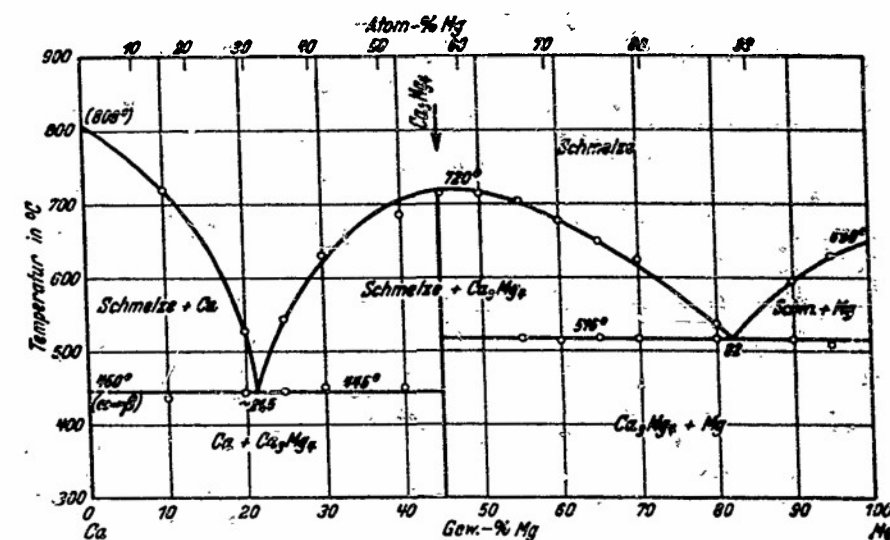


FIGURE 12. THE CALCIUM-MAGNESIUM SYSTEM, ACCORDING TO BAAR⁽²⁸⁾

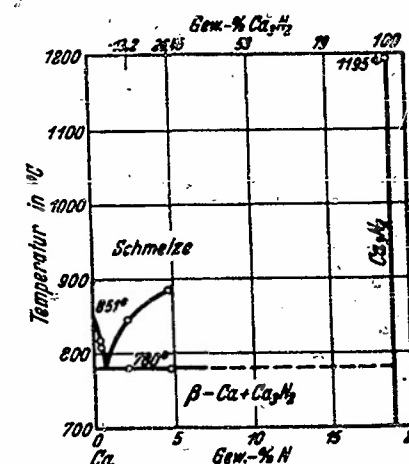


FIGURE 13. THE CALCIUM-NITROGEN SYSTEM, ACCORDING TO ANTROPOFF AND FALK⁽³⁵⁾

Antropoff and Falk⁽³⁵⁾ obtained calcium with 0.06% nitrogen and determined its melting point as $848^{\circ}\text{C} \pm 1^{\circ}\text{C}$, and calculated the value $851^{\circ}\text{C} \pm 1^{\circ}\text{C}$ as the melting point of chemically pure calcium. Later, Hoffmann and Schulze⁽³⁸⁾ obtained some very pure calcium prepared by W. Kroll in the Bel' Air Laboratory in Luxemburg, assaying 99.9% Ca. Spectroscopic determination of Al, Si, Mg, Fe, and C brought the balance to 100%. Nitrogen was determined as 0.01%. Both the melting point and freezing point of this sample were found to be 849°C . Other specimens with higher nitrogen content gave average values of 810°C , 813°C , and 819°C , but the melting points and freezing points did not check. By extrapolation, they agreed with Antropoff and Falk that the true melting point of calcium is $851^{\circ}\text{C} \pm 1^{\circ}\text{C}$. (Similarly, they determined the melting point of strontium as 771°C and barium as 704°C .)

Hansen⁽¹⁾ gives the data in Table 3 to indicate the effect of nitrogen on the melting point of calcium.

In view of these data, it must be pointed out that all of the earlier work by Donski and by Baar who alone have made serious attempts to investigate a wide range of high-calcium alloys, is of questionable accuracy, especially as to melting points (and it also affects solid solution ranges). Both Donski and Baar worked with calcium containing about 0.55% Al+Fe, 0.28% SiO_2 , and undetermined nitrogen. Their alloys were melted in Jena glass, which was attacked by the high-calcium alloys under hydrogen or no atmosphere. All of their high-calcium alloys were covered with oxide and scale.

TABLE 3. THERMAL ARRESTS OF CALCIUM, CALCIUM NITRIDE ALLOYS

Ca, %	Ca_3N_2 , %	N, %	Upper Arrest, $^{\circ}\text{C}$.	Lower Arrest, $^{\circ}\text{C}$.	Remarks
Distilled Ca	.03	0.06	—	848.4	—
97.4	2.6	0.49	817	809	Technical Ca: 0.25 Si, 0.15 Al, 0.26 Fe, 0.63 Mg, 0.66 MgCl_2
88.6	11.4	2.2	846	780	From sublimed Ca
74.6	25.4	4.8	887	780	From sublimed Ca
Ca_3N_2	100.0	18.9	—	1195	(39)

Nitrogen has no solid solubility in calcium, and forms no useful alloy.

Calcium-Sodium Alloys

Over the range 14% Na to 93% Na, two liquid layers are formed on melting. Hansen⁽¹⁾ gives the equilibrium diagram of Fig. 14, p. 50. The data are taken from Rinck⁽⁴⁰⁾ who used nitrogen-free calcium (melting point 848°C.) and Lorenz and Winger⁽⁴¹⁾ who used an impure calcium (melting point about 810°C.). The liquidus line at 710°C. was placed at 700°C. by Lorenz and Winger. Metzger⁽⁴²⁾, after melting sodium and calcium in a bomb at 900°C., found two layers in the regulus, one of which assayed 18% sodium, the other 80% sodium. Rinck reported that at 710°C., the composition of one layer is 7% Na in calcium, and the other is 14% Ca in sodium. He found a eutectic at 0.025°C. below the melting point of sodium. Extrapolation shows calcium and sodium to be miscible in all proportions above 1185°C. The inversion temperature from α -calcium to β -calcium at 450°C. does not appear to be affected by sodium.

Except as deoxidizers for certain other melts, calcium-sodium alloys would not be useful.

Calcium-Lead Alloys

The low-calcium alloys with lead have received considerable study which is reviewed quite fully by Mantell and Hardy⁽²⁾. 0.1% calcium (as CaPb_3) is soluble in lead at 328.3°C., while only 0.01% is

soluble at room temperature. As a result, the alloys found are age hardened. Age hardening takes place quite rapidly at room temperature.

The high-calcium alloys with lead have not been investigated thoroughly. Hansen⁽¹⁾ shows the diagram of Figure 15, taken from Donski⁽⁴³⁾ and Baar⁽⁴⁴⁾. No later determination is available. Donski and Baar both used calcium of the same grade, melting point 808°C., but Baar, using a hydrogen atmosphere, was able to melt higher calcium contents. He found a eutectic at about 39% lead (melting point 700°C.) between calcium and Ca_2Pb (melting point about 1110°C.). The existence of the γ -phase is somewhat doubtful. Donski placed a similar area of solid solution in the very similar calcium-tin diagram. Later, more careful work by Hume-Rothery did not bear this out. The compounds Ca_2Pb , CaPb , and CaPb_3 are well established.

The high-calcium alloys of this series are extremely unstable, corroding very rapidly in air.

Calcium-Antimony Alloys

The alloys of calcium with antimony were investigated by Donski⁽⁴⁵⁾ only in the range from 91% Sb to 100% Sb. He found a eutectic at 91.5% Sb, melting point 585°C. Nothing whatever is known of the rest of this system.

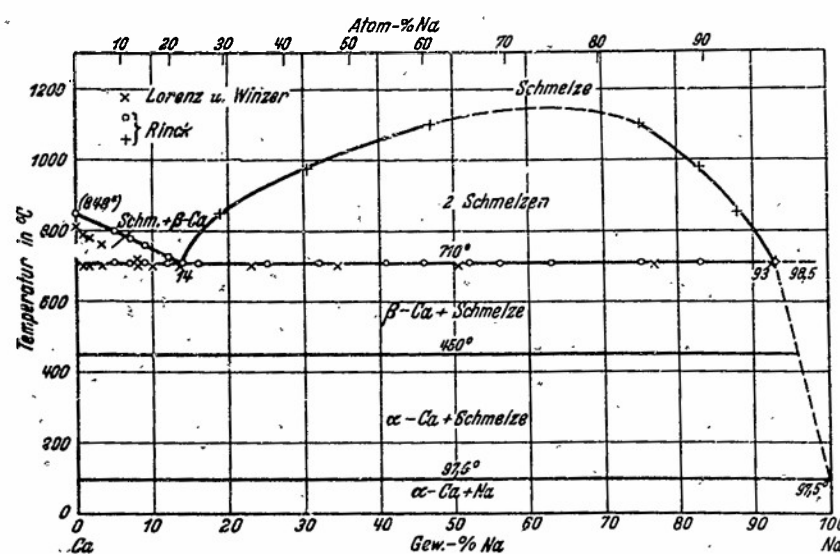


FIGURE 14. THE CALCIUM-SODIUM SYSTEM, ACCORDING TO RINCK⁽⁴⁰⁾

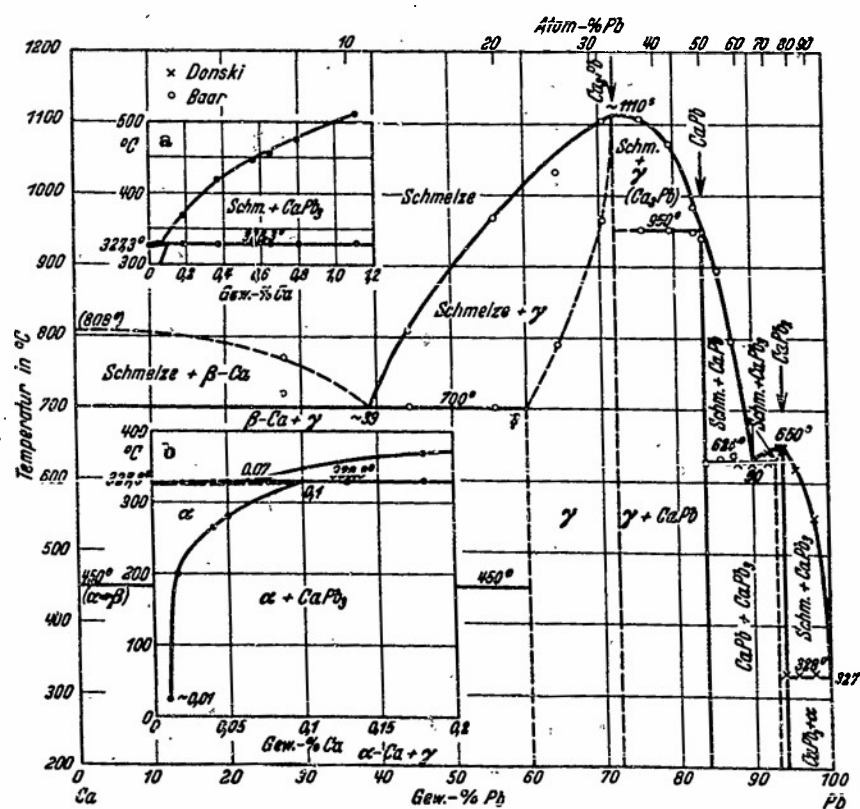


FIGURE 15. THE CALCIUM-LEAD SYSTEM, ACCORDING TO DONSKI⁽⁴³⁾ AND BAAR⁽⁴⁴⁾

Calcium-Selenium Compounds

Calcium selenide is a nonmetallic substance, formula CaSe_2 (66.41% Se). Metallic alloys may possibly exist, but nothing of importance is known of the high-calcium alloys of this system.

Calcium-Silicon Alloys

The literature contains a considerable number of references to this system of alloys, from F. Wöhler in 1863 to Louis and Franck in 1939. But only Tamaru⁽⁴⁶⁾ and L. Wöhler and Schliephake⁽⁴⁷⁾ have attempted to make a constitution diagram. The data points of both of these investigations are shown in Fig. 16, p. 53 from Hansen⁽¹⁾. Tamaru's alloys were strongly nitrided as he melted under a nitrogen atmosphere. He shows the melting point of calcium as 803°C. Wöhler and Schliephake used calcium 98.45% pure and silicon 99.48% Si. Their data are probably somewhat the better of the two.

Wöhler and Müller⁽⁴⁸⁾ heated calcium and silicon at 1000°C. and obtained Ca_2Si_2 . Heating Ca_2Si_2 in a stream of hydrogen at 1000°C. they obtained CaSi_2 . They claimed CaSi_2 could not be formed by fusion alone.

Louis and Franck⁽⁴⁹⁾ have substantiated the existence of CaSi , which forms at 1500°C., and is stable only at high temperatures, unless it is cooled rapidly (slow cooling allows decomposition into CaSi_2 and Ca), and Ca_2Si formed by direct fusion at 1000°C., which also breaks down on slow cooling.

From theoretical considerations, as noted in another section of this report, there is small likelihood of appreciable solid solution alloying of calcium and silicon because of the great difference in the size of the respective atoms.

These alloys are important deoxidizers in the steel and gray iron industries.

Calcium-Tin Alloys

The calcium-tin system has been quite carefully examined throughout the entire range by Hume-Rothery⁽⁵⁰⁾ as a part of his doctorate thesis. He used an argon atmosphere containing 10% nitrogen, but except for some lowering of the melting points at the high-calcium end, the diagram of Figure 17 from Hansen⁽¹⁾ is probably reliable. No evidence of solid solution has been found at either end of the diagram. Three compounds are formed: Ca_2Sn (59.70% Sn), CaSn (74.76% Sn), and CaSn_3 (89.89% Sn). Two eutectics are formed: one melting at 609°C. at 86% tin between CaSn_3 and CaSn_2 , and the other melting at 759° between Ca and CaSn_2 . There is no solid solution area between any of the compounds. Hume-Rothery found that the tin and calcium combine with explosive violence at the melting point of calcium. All of the high-calcium alloys corrode very rapidly in air, water, or acids.

Jenckel and Roth⁽⁵¹⁾ appeared to find a maximum solid solubility of calcium in tin of 0.1%.

The alloys have no commercial use.

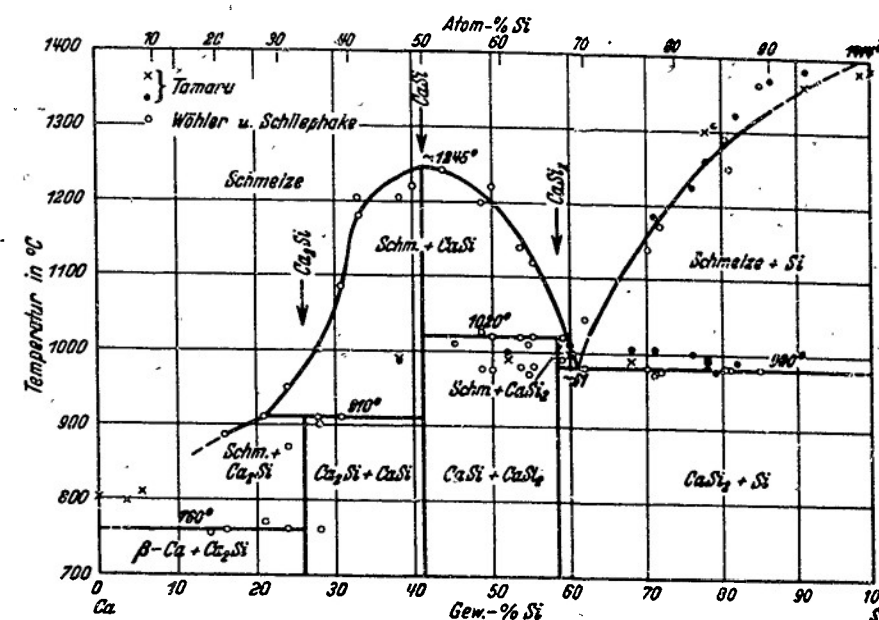


FIGURE 16. THE CALCIUM-SILICON SYSTEM, ACCORDING TO HANSEN⁽¹⁾

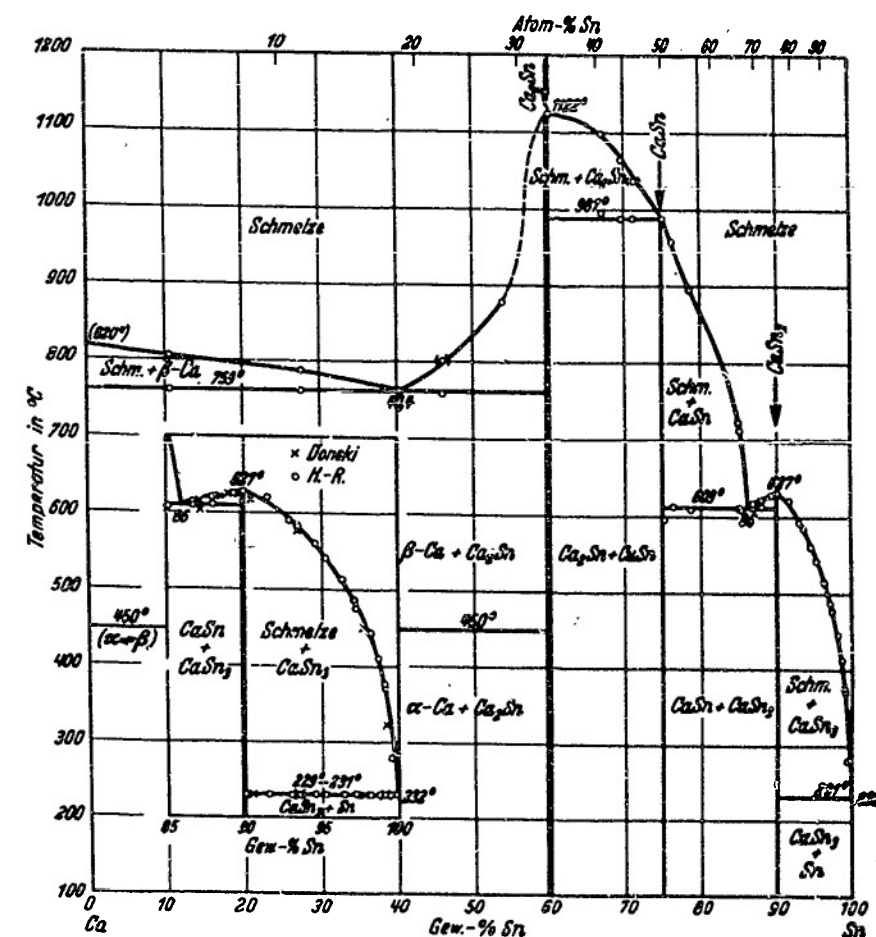


FIGURE 17. THE CALCIUM-TIN SYSTEM, ACCORDING TO HUME-ROTHERY⁽⁵⁰⁾

Calcium-Strontium Alloys

X-ray studies of calcium-strontium alloys have been made by Klemm and Mika⁽⁵²⁾ and by King⁽⁵³⁾. Both found a continuous series of solid solutions from 100% calcium (melting point 851°C.) to 100% strontium (melting point 771°C.).

Although an unlimited series of alloys is possible between these metals, the corrosion resistance of both is so similar and so poor that there would be no reason to expect any marked improvement in any alloy composition.

Calcium-Tellurium Alloys

The compound CaTe (76.09% Te) is nonmetallic, like CaSe. Oftedal⁽⁵⁴⁾ determined an X-ray lattice constant for CaTe of 6.345 ± 0.008 .

Calcium-Thallium Alloys

The investigation of the calcium-thallium series was begun by Donski⁽⁵⁵⁾ and carried forward by Baar⁽⁵⁶⁾, but is still incomplete. Hansen⁽¹⁾ gives the constitution diagram of Fig. 18, p. 56. Both investigators used calcium with 0.55% Al plus Fe, 0.28% Si, and undetermined nitrogen content. Baar made five cubic centimeter melts in glass under a hydrogen atmosphere. Starting with calcium (melting point 808°C.) the melting point falls slowly to 692°C. at about 63% thallium, where a eutectic between calcium and CaTl is found. A wide area of

solid solution of CaTl in calcium is indicated, but has not been determined accurately. Baar found some reaction taking place at 540°C. in the range from 23.6% Tl to 45% Tl, with the greatest energy emission at about 35% Tl, a reaction which he was unable to explain.

Besides CaTl (83.61% Tl), the compounds Ca_3Tl_4 (87.18% Tl) and CaTl_3 (93.87% Tl) were found. Baar determined the melting points of these compounds respectively as 970°C., 655°C., and 625°C.

Zintl and Neumager⁽⁵⁷⁾ found the crystal lattice structure of CaTl_3 similar to that of CaPb_3 . Zintl and Braner⁽⁵⁸⁾ reported a cubic body-centered lattice structure for CaTl, similar to β brass.

Calcium-Tungsten Alloys

According to Kremer⁽⁵⁹⁾, it is not possible to alloy calcium and tungsten.

Calcium-Zinc Alloys

The only complete diagram available is that given in Hansen⁽¹⁾ from the work of Donski⁽⁶⁰⁾, and here reproduced as Figure 19. Donski himself pointed out that he might not have found all of the compounds, and that the compound CaZn (62.0% zinc) was very doubtful. Evidently more work is necessary in the calcium-rich calcium-zinc alloys. Donski found a eutectic at 43.5% Zn melting at 417°C. between calcium and a compound tentatively identified as CaZn , and another eutectic at 83.5% Zn (melting point 633°C.) between Ca_2Zn_3 and CaZn_{10} . He showed

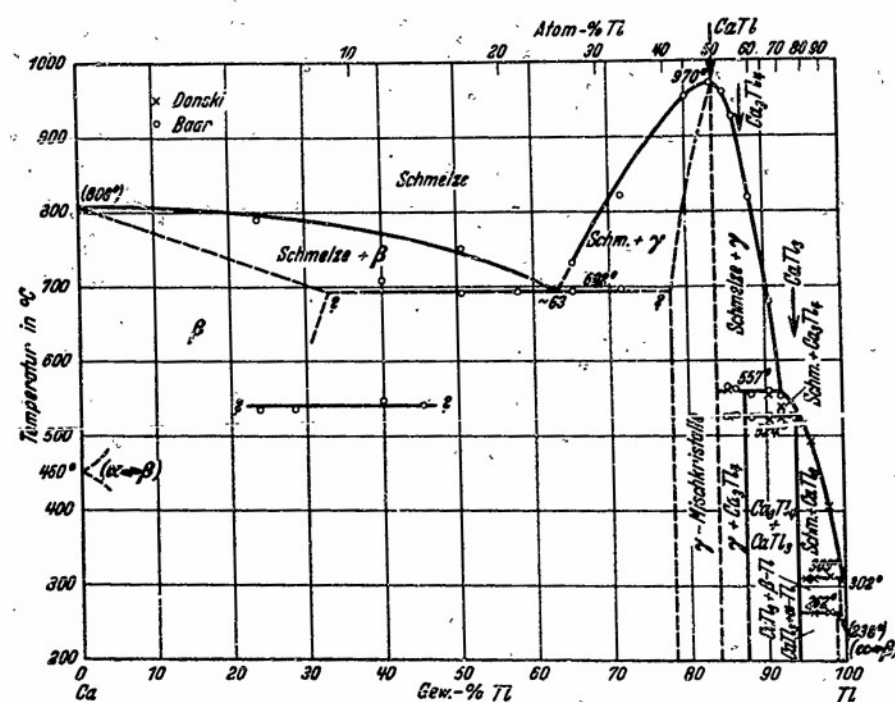


FIGURE 18. THE CALCIUM-THALLIUM SYSTEM, ACCORDING TO DONSKI⁽⁵⁵⁾ AND BAAR⁽⁵⁶⁾

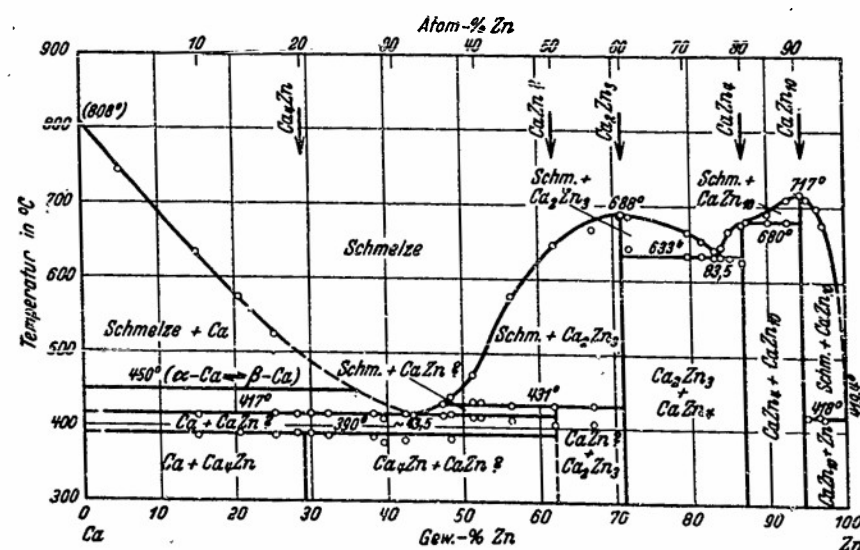


FIGURE 19. THE CALCIUM-ZINC SYSTEM, ACCORDING TO DONSKI⁽⁶⁰⁾

compounds: Ca_4Zn (28.97% Zn), CaZn (62.0% Zn), Ca_2Zn_3 (70.99% Zn), CaZn_4 (86.71% Zn), and CaZn_{10} (94.23% Zn). Kremann, Wostall, and Schöpfer⁽⁶¹⁾ found the compounds CaZn , Ca_2Zn_3 , CaZn_4 , and CaZn_{10} by means of potential measurements. Roos⁽⁶²⁾ determined the heats of fusion and of formation of CaZn_4 and CaZn_{10} : CaZn_4 - heat of fusion 83.5 cal./g., heat of formation 55.6 ± 3 cal./g.; CaZn_{10} - heat of fusion 79.6 cal./g., heat of formation 199.1 ± 4.7 cal./g. He notes that CaZn_4 is an exception to the rule that heat of formation increases with heat of fusion in the compounds he examined.

Haucke⁽⁶³⁾ examining the crystal structure of CaZn_4 and CaCu_4 came to the conclusion that the compounds were really CaZn_5 and CaCu_5 . Both crystallize in similar hexagonal lattices of symmetry, group $D6\lambda$, with six atoms in the unit cell. For CaZn_5 , $a = 5.405$, $c = 4.183\text{\AA}$; for CaCu_5 , $a = 5.082$, $c = 4.078\text{\AA}$. This structure gives Zn and Cu a coordination number of 12.

Nowotny⁽⁶⁴⁾ also determined the X-ray structure of CaZn_5 and CuZn_5 , for which he found values as follows: Ca_5Zn , $a = 5.371$, $c/a = 1.579$, $d = 5.72$; for CaCu_5 , $a = 5.097$, $c/a = 1.579$.

Mantell and Hardy⁽²⁾ note that calcium-zinc alloys and calcium-magnesium-zinc alloys are suggested for use in the production of porous concrete. A 50-50 zinc-calcium alloy and a 15 zinc, 15 magnesium, 70 calcium alloy are most suitable. The alloys are very brittle, highly reactive, and spontaneously combustible. All of the ternary zinc-magnesium-calcium alloys containing 30% or more of calcium oxidize readily.

No structural alloys with a calcium base containing zinc are probable.

Calcium-Zirconium Alloys

Except in the alloys of nickel patented by Lohr⁽⁶⁶⁾, no reference to calcium-zirconium alloys was found. Lohr's alloys contained 0.01 to 0.20% calcium, 0.01 to 1.0% zirconium, 10 to 25% chromium, with varying amounts of iron and molybdenum (0% to 30%), balance nickel. Mantell and Hardy⁽²⁾, page 107, give a list of these alloy compositions.

DISCUSSION

Examination of the available literature has shown very little promise of a possible high-calcium alloy that would be stable in air or water. The addition of a small amount of magnesium is said to improve the mechanical properties and stabilize the metal somewhat.

The alloys with barium, strontium, and Misch metal (cerium plus lanthanum, etc.) might be investigated for possible stabilizing effects.

From a theoretical standpoint, much careful study of the high-calcium alloys remains to be done, but it is doubtful that useful structural alloys with good corrosion resistance can be obtained.

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